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PVC membrane lithium-selective electrodes based on oligomethylene-bridged bis-1,10-phenanthroline derivatives

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Abstract

Poly(vinyl chloride) (PVC) membrane electrodes are prepared for lithium, based on several kinds of synthesized oligomethylene bridged bis-1,10-phenanthroline derivatives as neutral carriers. Potassium tetrakis(*p*-chlorophenyl)borate (KTCPB) and tetrakis(*p*-fluorophenyl)borate (TFPB) as lipophilic salts were added into the membranes to improve the selectivity for lithium over alkali and alkaline earth metal ions. The effects of different plasticizers on the electrode performance are discussed. The relationship between the impedance of electrodes and their performance are analyzed, and the membrane composition of the electrode was optimized. The electrode with the optimal membrane composition showed a $\log K^{Pot}_{Li,Na}$ value of −3.2 (1700 times more selective to lithium ion over sodium ion).

Keywords: Ion-selective electrode; Lithium ion; Oligomethylene bridged bis-1,10-phenanthroline derivatives; Impedance

1. Introduction

Studies of lithium-selective electrodes have recently attracted much attention of many researchers for the determination of lithium ion activity in biological and environmental systems, e.g., in the therapy of manic depressive psychosis [1–3]. There are many reports [4–11] concerning the studies of lithium-selective electrodes. As one knows, there are very few naturally occurring antibiotics that have high selectivities against sodium ion for practical use so far. Therefore, much efforts have been focused on the synthesis of cyclic [6–10] and non-cyclic [4,11,12] neutral carriers with sufficient ability to complex Li^+.

1,10-Phenanthroline derivatives are generally used as complexing agents for transition metal ions such as Cu^+ [13] and Fe^{2+} [14]. They also form complexes with alkali and alkaline earth metal ions [15], but few have been described as neutral carriers for use in ion-selective electrodes [16]. The present authors reported lithium ion-selective electrodes based on 1,10-phenanthroline derivatives such as 2,9-dimethyl-1,10-phenanthroline and 2,9-dibutyl-1,10-phenanthroline which show excellent selectivity for lithium ion over other alkali and alkaline earth metal ions [17–19]. NMR titration demonstrates that 2,9-dibutyl-1,10-

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phenanthroline forms a 2 : 1 ligand : metal complex with Li^+ in solution [20]. The impedance measurement of the poly(vinyl chloride) (PVC) membranes, with some of the optimized plasticizers as solvent mediators for the carrier 2,9-dibutyl-1,10-phenanthroline, inferred that the ion-carrier complex formation process was the major step which discriminated Li^+ against other ions [19].

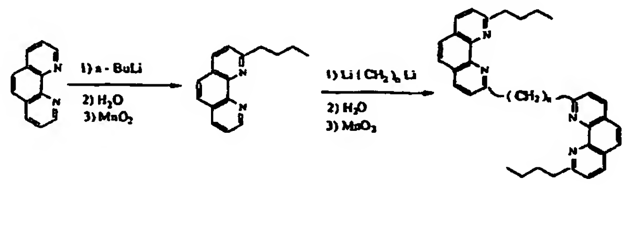
A series of new compounds have also been synthesized which consist of two phenanthrolines bridged with an oligomethylene chain and which can form 1 : 1 complexes with Li^+, for the purpose of preparing highly selective neutral carriers for Li^+ [21]. The characteristics of ion transport in the chloroform liquid phase incorporated with these new compounds were discussed, and it was found that there was an optimum chain length for the oligomethylene bridge in order to have the most favorable orientation for the 1 : 1 Li^+-carrier complex [21].

In this work, the effects of various different carriers, additives, plasticizers and proportions on electrode performance are examined using these oligomethylene bridged phenanthroline derivatives. The membrane compositions of the electrodes are optimized. The impedance of the electrodes are investigated as well for different ions and concentrations. The electrodes prepared from the new compounds exhibit excellent selectivity.

2. Experimental

2.1. Materials

1,4-Bis(9-butyl-1,10-phenanthrolin-2-yl)butane (1), 1,5-bis(9-butyl-1,10-phenanthrolin-2-yl)pentane (2), 1,6-bis (9-butyl-1,10-phenanthrolin-2-yl)hexane (3), 1,7-bis(9-butyl-1,10-phenanthrolin-2-yl)heptane (4) and 1,8-bis(9-butyl-1,10-phenanthrolin-2-yl)octane (5) were synthesized from 2-butyl-1,10-phenanthroline (which was prepared by using 1,10-phenanthroline and *n*-butyl lithium [22]) and α,ω-dilithioalkane in the following way [23]:



The plasticizers used in the present paper were *o*-nitrophenyl octyl ether (NPOE), *o*-nitrophenyl phenyl ether (NPPE) and 1-fluoro-1′-nitrodiphenyl ether (FNDPE). These were available commercially from Dojindo Laboratories, Kumamoto, Japan, and were used without further purification.

Poly(vinyl chloride) (PVC, average degree of polymerisation 1100) was also commercially available from Wako Pure Chemical Industries, Tokyo. It was preliminarily purified by precipitation from tetrahydrofuran (THF) in methanol.

Both potassium tetrakis(*p*-chlorophenyl)borate (KTCPB) and tetrakis(*p*-fluorophenyl)borate (TFPB) were used as lipophilic additives in order to improve the selectivity for lithium over alkali metal ions. All reagents were of analytical grade unless otherwise stated. Water used was deionized (specific conductance $<5\times10^{-7}\,\Omega^{-1}\,cm^{-1}$).

2.2. Preparation of electrodes

The PVC membrane electrodes were prepared as follows: the carrier (5 mg), plasticizer (250 mg), PVC (100 mg) and lipophilic additive (3 mg) were dissolved in 4 ml of THF. The solution was poured into a petridish (42 mm diameter) which was placed horizontally on a mercury pool. The THF was slowly evaporated over about 24 h at room temperature to obtain a yellow, transparent, flexible membrane of ca. 0.2 mm thickness. A disk of 5 mm diameter was cut from the membrane and was mounted into a PTFE electrode body (which had a diameter of 13 mm and a length of 120 mm) for emf measurements.

2.3. emf measurements

An internal solution of 0.01 mol dm^{-3} LiCl and a Ag/AgCl internal reference electrode were used. The PVC membrane electrode prepared was conditioned by soaking in 0.01 mol dm^{-3} LiCl solution for about 1 h before measurements were made. The external reference electrode was a double jacket silver–silver chloride electrode in which the solution in the inner tube was saturated KCl and in the outer tube was 0.1 mol dm^{-3} NH_4NO_3. The electrochemical cell

used for measurements is as follows:

Ag|AgCl|0.01 mol dm^{-3}LiCl||PVC membrane|| sample solution|0.1 mol dm^{-3}NH_4NO_3|satd. KCl|AgCl|Ag.

The sample solutions were prepared from analytical-reagent grade chlorides of alkali and alkaline earth metals and deionized water. The potentiometric ion-selectivity coefficients $K_{i,j}^{\mathrm{Pot}}$ (i is the primary ion; j is an interfering ion) were determined by the separate-solutions method [24], using the Nicolsky–Eisenman equation as follows:

$$E = E_i^0 + \frac{2.3RT}{Z_iF}\log\left[a_i' + \sum_{i \neq j} K_{i,j}^{\mathrm{Pot}}(a_j')^{Z_i/Z_j}\right],$$

where, R, T, F, Z and a denote the gas constant, absolute temperature, Faraday constant, charge of the ion and ionic activity, respectively [25]. A computer-aided automatic testing apparatus [26] was used for the measurement of emf and data processing. For some of the membranes, the mixed solutions method with fixed interferent levels (for NaCl 0.14 mol dm^{-3} and 1 mol dm^{-3}, for KCl 1 mol dm^{-3} and for $CaCl_2$ 0.1 mol dm^{-3}) was also adopted in order to obtain the ion-selectivity coefficients $K_{i,j}^{\mathrm{Pot}}$ and to compare them with those obtained by the separate solutions method.

Impedances of electrodes were measured with a symmetric double electrode (Ag|AgCl|10^{-4}–0.1 mol dm^{-3}MCl| PVC membrane |10^{-4}–0.1 mol dm^{-3}MCl|AgCl|Ag) cell [19]. The area of the membrane contacting the aqueous solution was 0.65 cm^2. A SI 1260 Impedance/Gain-Phase Analyzer coupled with a PC-9801 VM computer was used for the measurement and analysis of the impedance of the Li^+ ion-selective electrodes.

3. Results and discussion

3.1. The potentiometric response characteristics and durability of the electrode

Fig. 1 shows the calibration graphs for Li^+ of PVC membrane electrodes using NPOE or FNDPE as plasticizers under fixed interferent conditions. The lithium ion-sensitive electrode prepared by using carrier **3** with the NPOE solvent mediator and the KTCPB lipophilic additive according to the optimum membrane composition showed a potentiometric response described by the equation:

$$E = 247 + 56.4\log a \quad (r = 0.99, n = 6) \tag{1}$$

with a linear response range from 1.0×10^{-4} to 1 mol dm^{-3} and an average slope of 56.4 mV/decade. The limit of detection was 9.5×10^{-5} mol dm^{-3}. The response characteristics and the lithium selectivity over other ions were reproduced for three days if the electrodes were conditioned in 10^{-2} mol dm^{-3} LiCl all the time after the measurements (see Table 1). However, they began to deteriorate slowly after four days.

3.2. The effect of solvent mediator and carrier on electrode performance

The effect of several solvent mediators and carriers on electrode performance was examined. Fig. 2 summarizes the results obtained with membranes containing KTCPB as a lipophilic additive and five kinds of carriers (**1–5**), with NPOE, FNDPE and NPPE as plasticizers. It seems that the electrodes with NPOE as plasticizer give the best selectivity to Li^+ compared to FNDPE and NPPE. In Fig. 2 (a) electrodes based on carriers **3**, **4**, **5** and plasticizer NPOE exhibit excellent selectivity for lithium ion over other metal ions. The selectivity coefficients $\log K_{\mathrm{Li,Na}}^{\mathrm{Pot}}$ of the electrodes for lithium over sodium (calculated by the iso-activity method of separate solutions at 1 mol dm^{-3}) based on carriers **1**, **2**, **3**, **4**, **5** are −2.70, −2.48, −3.23, −3.06 and −3.07, respectively (the uncertainty is 2–3%). This means that carriers with too short (e.g. **1**, **2**) or too long (e.g. **4**, **5**) chains to bridge phenanthroline moeties are not good for the improvement of selectivity for Li^+ over other metal ions [21]. Carrier **3** gives the best selectivity among all five carriers. The selectivity value −3.23 (1700 times preference for Li^+ over Na^+) found for carrier **3** in combination with the plasticizer NPOE proves to be the best among so far reported carriers which form 1 : 1 complexes with Li^+. The selectivity value was somewhat smaller when the mixed solutions method was used, and $\log K_{\mathrm{Li,Na}}^{\mathrm{Pot}}$ was

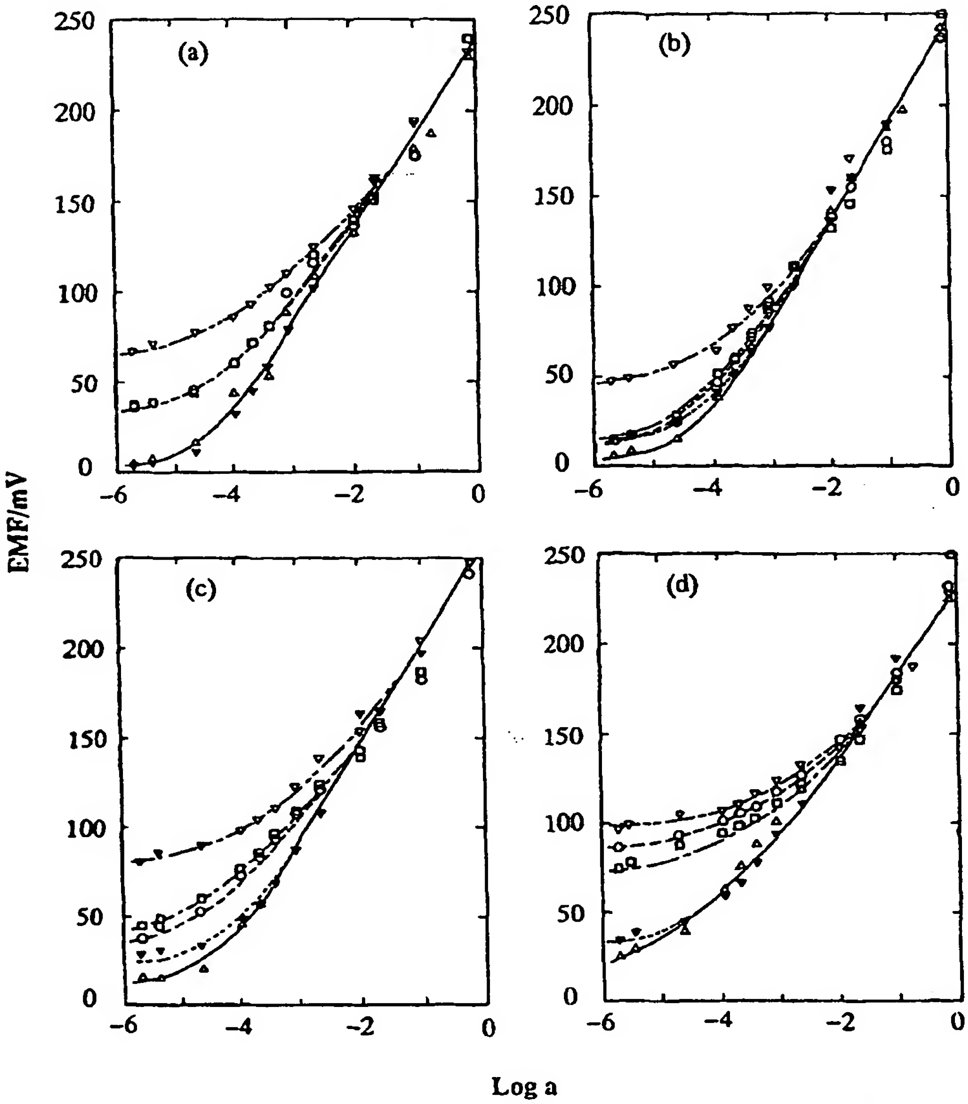


Fig. 1. Calibration graphs for Li^+ of PVC membrane electrodes based on carrier 3 using NPOE or FNDPE as plasticizers under fixed interferent conditions. △, No interferent; ▽, 1 mol dm^{-3} NaCl; □, 0.14 mol dm^{-3} NaCl; ○, 1 mol dm^{-3} KCl; ▼, 0.1 mol dm^{-3} $CaCl_2$. Membrane compositions: (a) 0.8% m/m carrier 3, 70.2% m/m NPOE, 0.8% m/m KTCPB, 28.1% m/m PVC; (b) 1.4% m/m carrier 3, 69.8% m/m NPOE, 0.8% m/m KTCPB, 27.9% m/m PVC; (c) 2.8% m/m carrier 3, 68.9% m/m NPOE, 0.8% m/m KTCPB, 27.5% m/m PVC; (d) 1.4% m/m carrier 3, 69.8% m/m FNDPE, 0.8% m/m KTCPB, 27.9% m/m PVC.

found to be −3.1 for the carrier 3 in combination with NPOE (the uncertainty was 5–8%, see also Table 2). The tendency was similar and somewhat marked when FNDPE was used as a plasticizer. In NPPE, the oliomethylene chain length for the appearance of the best lithium selectivity was a little longer compared with NPOE or FNDPE.

3.3. The effect of additives on electrode performance

Different additives were tested (Fig. 3). As illustrated in Fig. 3, the additive KTCPB gives rise to a better response behavior than TFPB. It should be noticed that in both the electrodes where there is no special additive (see Fig. 3(c)) and no special carrier,

Table 1
Durablity tests of the Li^+-selective electrode based on carrier 3 with NPOE as a plasticizer. Lithium selectivity coefficients are obtained by the separate solutions method

Run	Time in days	Slope (mV) of emf-log$a$ curve	$\log K^{Pot}_{Li,M}$					
			H^+	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
1	initial	56	2.57	0	−3.23	−3.75	−3.25	−3.35
2	1	56	2.46	0	−3.21	−3.68	−3.10	−3.18
3	3	54	2.43	0	−3.21	−3.60	−3.07	−3.19
4	4	51	2.37	0	−3.11	−3.40	—	−3.32
5	5	51	—	0	−3.10	−3.36	−2.79	−2.96
6	6	51	2.35	0	−3.04	−3.26	−2.55	−2.86

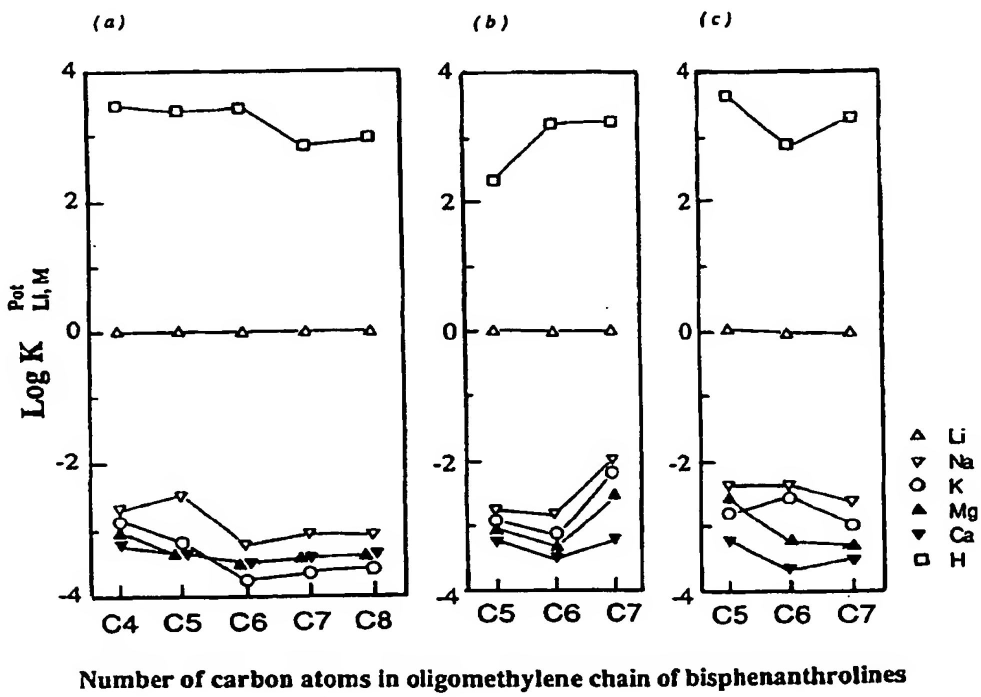


Fig. 2. Selectivity coefficients of PVC membranes containing various dimers of 1,10-phenanthroline derivatives as carriers with different plasticizers: (a) NPOE, (b) FNDPE, (c) NPPE.

i.e., only contains additive KTCPB (see Fig. 3(d)) show very poor electrode performance for Li^+. Therefore, KTCPB was utilized as the additive in the following experiments.

3.4. The optimization of electrode membrane composition

In order to prepare the electrode which has optimum response performance to Li^+ by means of given materials, the membrane composition of the electrode was optimized. The results are listed in Table 2 (see also Fig. 1). As shown in Table 2, the optimum membrane composition of the Li^+-selective electrode is as follows: 1.4% m/m carrier 3, 69.8% m/m NPOE, 0.8% m/m KTCPB and 27.9% m/m PVC. It should be noted, however, that deterioration of membranes would occur if the membranes were subjected to slow dissolution of components, resulting in the change in membrane compositions, as

Table 2
Optimization of membrane composition for Li^+-selective electrode. Lithium selectivity coefficients are obtained by the separate solutions method

No.	Weight (mg)				$\log K^{Pot}_{Li,M}$					
	Carrier (3)	Plasticizer (NPOE)	Additive (KTCPB)	PVC	H^+	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
1	3	250	3	100	2.32	0	−2.00 (−2.6)	−2.08 (−3.5)	−3.19	−3.36 (−3.7)
2	5	250	3	100	3.45	0	−3.23 (−3.1)	−3.71 (−3.6)	−3.48	−3.48 (−3.3)
3	5	250	0	100	2.29	0	−0.29	−0.42	−1.13	−1.33
4	10	250	3	100	2.83	0	−2.97 (−2.8)	−3.47 (−3.4)	−3.62	−3.71 (−3.5)

Values in parentheses are those obtained by the mixed solutions method.

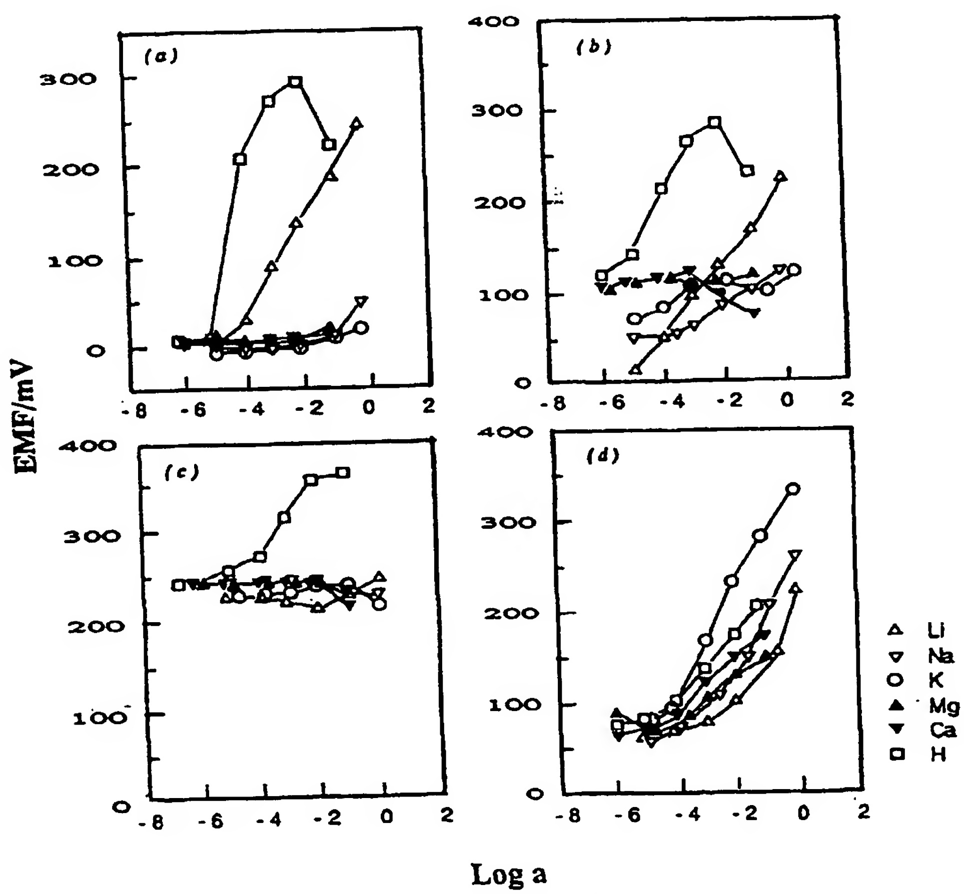


Fig. 3. Calibration graphs for electrodes with PVC membranes containing carrier 3 and various kinds of lipophilic additives in plasticizer NPOE. (a) KTCPB, (b) TFPB, (c) no additive, (d) KTCPB is used to replace carrier.

might be inferred from Tables 1 and 2. Special research efforts should be directed in order to maintain membrane durability against this kind of deterioration.

3.5. Measurement and analysis of the impedance of the electrodes

The impedance method is a useful tool to investigate ion transport in plasticized PVC membranes with neutral carriers [19,27–30]. In this paper, the relationship between impedance and response characteristics of the Li^+ ion-selective electrodes was studied with various membrane compositions.

Different electrodes have different resistances and geometric capacitances. In order to investigate the relationship between the carrier and impedance of the electrode, the specific resistance of the bulk membrane was measured against carriers of electrodes in solutions containing ions Li^+, Na^+ or K^+. In general, the specific resistance and capacitance of membranes in a Li^+ solution were less than those in Na^+ and K^+ solutions except in a few cases. It appears that the membrane based on carrier **3** has a slightly lower specific resistance than carrier **2** or **4**. From this it can be anticipated that carrier **3** takes the most C orientation with Li^+ ions and that the Li^+-carrier complex is the smallest, which results in the fastest transport in the membrane phase. It is very important that the electrode which does not contain any additive in the membrane has a relatively high resistance compared to others such as the electrodes containing additive KTCPB or TFPB as shown in Fig. 4. Furthermore, KTCPB is preferable to TFPB as the electrode based on the former has a lower specific resistance. This means that the additive can decrease the impedance of the electrode and improve the Li^+ ion transport behavior in the membrane.

If one compares the impedances of electrodes based on plasticizers NPOE, NPPE and FNDPE, the membrane bulk impedance increases by the following sequence: $R_{NPOE} < R_{NPPE} < R_{FNDPE}$ as demonstrated in Fig. 5. This shows that NPOE can promote Li^+ ion transport in the membrane better than NPPE and FNDPE. These features should be compared with the case in membranes containing 2,9-dibutyl-1,10-phenanthroline forming a 2 : 1 complex with Li^+ [19], where the transport rate of the lithium-carrier complex in the membrane had very poor correlation with the observed sequence of lithium selectivity of the electrode. Note, however, that only the membrane bulk resistances can be compared in the impedance measurements, and they do not correspond directly

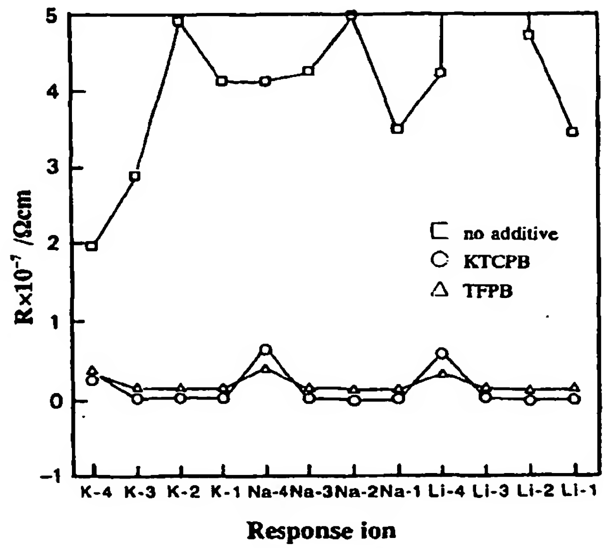


Fig. 4. Effect of additives on the specific resistance of membranes with plasticizer NPOE containing carrier 3. Solution abbreviation: K-4: 1×10^{-4} mol dm^{-3} KCl; K-3: 1×10^{-3} mol dm^{-3} KCl; K-2: 1×10^{-2} mol dm^{-3} KCl; K-1: 0.1 mol dm^{-3} KCl, etc.

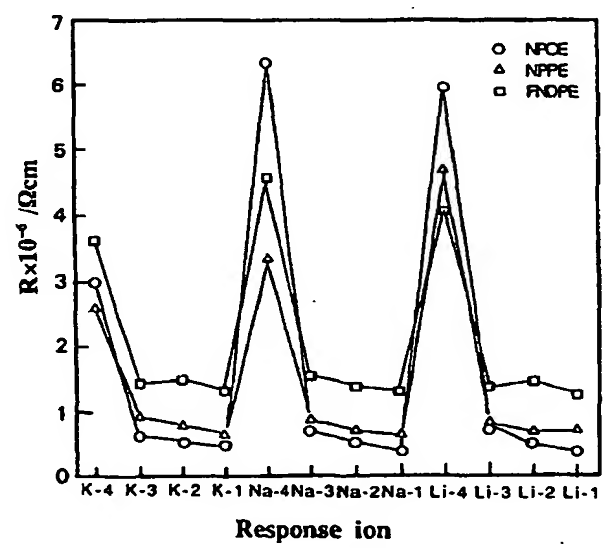


Fig. 5. Effect of plasticizers on the specific resistance of membranes based on carrier 3. Solution abbreviations as in Fig. 4.

with the potentiometric selectivities for Li^+ over other ions measured on ion-selective electrodes. The ion-carrier complex formation step is assumed to be the dominant contribution to the appearance of Li^+-selectivities [19].

The effects of electrode membrane composition based on carrier 3, plasticizer NPOE and additive KTCPB on impedance were studied. It was shown that specific resistances of electrodes with different membrane compositions are very similar except the membrane which has no additives. On the whole, the results obtained by impedance measurements and analyses are in qualitative accordance with those obtained by the selectivity and response characteristics studies of membranes in so far as the rate of the transport process through the membrane is correlated with the membrane impedance.

4. Conclusions

In this paper, membrane electrodes based on oligomethylene-bridged bis-1,10-phenanthroline derivatives as neutral carriers are studied for lithium ion. The effects of carriers, plasticizers and additives on electrode characteristics are discussed in detail. The correlations between impedance and performance of electrodes are analyzed. The optimal membrane composition of the electrode is 1.4% m/m carrier 3, 69.8% m/m NPOE, 0.8% m/m KTCPB, 27.9% m/m PVC. The electrode with the optimal membrane composition showed an excellent lithium to sodium selectivity value $\log K^{\mathrm{Pot}}_{\mathrm{Li,Na}}$ of −3.2 which, as a neutral carrier forming a 1 : 1 complex with Li^+, is superior to those reported so far. It is worthy of further studies on the relationship among structures of carriers, selectivities, membrane durabilities and impedance of electrodes, in order to find new carriers with satisfactory performances.

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